

Surface reactions of metal clusters. II. Reactivity surveys with D₂, N₂, and CO

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Reactions on the surface of a variety of transition metal clusters have been studied in the gas phase at near room temperature using a newly developed fast-flow reaction device. Initial examples of the use of this device are provided by survey studies of the reactivity of iron, cobalt, nickel, copper, and niobium clusters in contact with low concentrations of D₂, N₂ and CO. Dissociative chemisorption of D₂ is found to occur with dramatic sensitivity to cluster size in the cases of iron, cobalt, and niobium clusters, the detailed pattern of reactivity differing markedly for each metal. The corresponding reaction is also observed with nickel clusters, but here the reactivity shows only a slow, steady increase with cluster size. Copper clusters are found to be completely unreactive to H₂ chemisorption under these conditions. Molecular nitrogen is found to chemisorb readily to clusters of cobalt and niobium, with a reactivity pattern very similar to that observed with D₂. Iron clusters are found to show slight reactivity with N₂; only a small amount of chemisorption is observed on the most reactive clusters at high N₂ concentration, but the pattern of this reactivity with cluster size is consistent with that observed in D₂ chemisorption. In contrast to these highly structured reactivity patterns of D₂ and N₂, carbon monoxide is found to show only a slow, monotonic increase in reactivity with cluster size. It is suggested that these dramatic reactivity patterns for chemisorption on metal clusters provide stringent tests for future theories as to the nature of chemisorption on metal surfaces at a detailed, molecular level.

I. INTRODUCTION

Paper I of this series¹ introduced a new fast-flow chemical reactor scheme which enables the surface reactivity of metal clusters to be studied in a general and powerful way. This second paper now presents results of an initial survey of the application of this new technique to a variety of transition metal clusters in their reactions with D₂, N₂, and CO. An initial communication of a portion of the D₂ chemisorption results on cobalt and niobium clusters has appeared earlier in this Journal.²

The chief motivation behind this series of papers is the prospect of a new alternative for the study of chemistry on surfaces—particularly the important chemistry that is unique to heterogeneous catalysis. Over the past 10–15 years, advances in ultrahigh vacuum (UHV) technology together with an arsenal of new surface-sensitive probes produced a new paradigm³ for the study of heterogeneous catalysis^{4–8}: study of the single crystal surface in UHV. Although oversimplified in many aspects, the single crystal provides a useful model of real polycrystalline surfaces while retaining the advantages of high symmetry, repeatability, and relative ease of characterization. This single crystal in UHV is certainly not the only model relevant to heterogeneous catalysis, however. There are other conceivable models, and of these the bare metal cluster in UHV is particularly appealing.

Traditionally there have been two fairly distinct theoretical approaches to surface chemistry: the infinite slab and

the molecular cluster.^{9–12} The first of these is an adaptation of band theory, emphasizing the delocalized electron motion of an infinite two dimensional slab. In a typical calculation this slab would be composed of a small number of atomic layers of the bulk solid together with a layer of interacting molecules regularly disposed both above and below the surface. An elementary but particularly interesting example of such a slab calculation can be found in a recent paper of Saillard and Hoffman¹³ which uses extended Hückel theory to discuss the dissociative chemisorption of H₂ on a slab of nickel four monolayers thick. In contrast, the molecular cluster approach largely ignores the long wave effects so well treated with band theory, and focuses attention on the short range, molecular interactions among a small number of atoms at the surface. For example, Siegbahn, Blomberg, and Bauschlicher¹⁴ have recently presented SCF calculations with very extensive CI for the case of hydrogen dissociative chemisorption at various sites on small clusters of nickel.

Of these two, the surface cluster approach clearly has potential for a more detailed theoretical understanding of the chemistry occurring at a particular reactive surface site. An intrinsic problem with the cluster approach is the need to correct for long wave phenomena introduced by embedding this cluster in the bulk surface. In principle, such long range bulk effects could be included simply by calculating clusters of successively larger sizes. Unfortunately, it turns out that the cluster size sufficient to accurately mimic bulk surface behavior is often hopelessly large.

As a result there has been an inherently poor coupling between theory and experiment in surface chemical studies. The theory is best done on the small clusters, whereas (up to now) the best, most definitive experiments applied only to the bulk single crystal surface. Because of its potential for a

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more intimate coupling to theory, the bare metal cluster is in many respects a preferable model of a real catalytic surface than is the single crystal.

In fact, it is becoming increasingly clear that there is a remarkable parallel between the bare metal cluster and single crystal experiments in surface science. Just as it is possible to obtain pure single crystals of almost any metal, with the new laser vaporization techniques^{15–18} it is now routine to generate bare cluster beams of any metal in the Periodic Table. Both experiments use high vacuum to ensure that the surface remains clean during analysis (although since the analysis time is shorter, the requisite vacuum quality in the case of clusters is not nearly so high as in surface studies). One-photon direct laser ionization, followed by mass spectral analysis, gives a means of assessing the purity of the cluster as well as its identity—much the same as Auger spectroscopy does for bulk surface experiments. And now, through the use of the fast-flow reactor of paper I in this series,¹ it is possible to expose these clusters to reactants under known and controllable temperature, pressure, and contact time, and then to suddenly transport them into high vacuum for laser analysis of the chemistry that has occurred. This is a near perfect analogy to the recent practice of transporting a well-characterized single crystal sample from UHV conditions into a high pressure reactor, and then returning to the UHV chamber to characterize the resulting surface chemistry.

The following sections present the details of an initial coarse survey of the sort of reactivity patterns to be observed with the new fast-flow reactor device. We were particularly interested in finding very large, qualitative variations in cluster reactivity with cluster size and composition—effects so large as to be clearly and definitively established even in this rather crude, early youth of the cluster beam technique. As documented below, such effects were found in abundance.

II. EXPERIMENTAL

Paper I of this series has described in extensive detail the fast-flow metal cluster reactor used in this work.¹ In brief, this device utilizes a pulsed laser to vaporize an appropriate metal target in the throat of a supersonic nozzle. Metal clusters formed in the helium carrier gas of this nozzle then flow into a downstream reaction tube where shock waves and mixing with turbulent boundary layers warm the gas and clusters back to near 320 K. Reactants diluted in helium are concurrently injected into the reaction tube, where they interact with the clusters for 150–200 μ s before the gas freely expands out of the reaction tube, forming an intense supersonic beam. During the reaction contact time the average density of helium buffer gas is in the range of 50 to 100 Torr, which is sufficient to thermalize any reaction product within a few microseconds.

The result of the reaction was monitored by examining the resultant supersonic beam by direct photoionization with an F_2 excimer laser followed by time-of-flight mass-selective detection of the cluster photoions.

Reagents were metered through a Hastings–Teledyne digital flowmeter, merged with a flow of pure helium, and the resultant mixture passed through a catalytic purifier

(Airco model 98) which also served to ensure excellent mixing of the reactant. Even though the fast-flow reactor design supported up to four independent pulsed reaction nozzles, only two were used in the present study. One always contained pure helium at the same pressure (3.8 atm) as the reactant gas mixture. The two reactant nozzles were driven by the same pulsed power supply, running under computer control so that pulses of reactant gas alternated with pulses of pure helium as a control. The two nozzles were carefully matched to produce the same effective flow during their 2–3 ms pulse durations. The gas lines leading to these nozzles were valved such that either nozzle could serve as the control. At the beginning of each experimental session, a nozzle matching experiment was performed using pure helium in both nozzles, and the measured TOFMS cluster distribution obtained from each nozzle was recorded. Generally the nozzles were sufficiently well matched that no significant difference was noted in the respective cluster distributions.

III. RESULTS AND DISCUSSION

Since each has only one naturally occurring isotope, niobium and cobalt are particularly convenient metals for an initial survey of metal cluster reactions using the new technique. In what follows we focus initially on the reactions of a few simple small molecules with these single-isotope metal clusters; later we discuss the corresponding reactions with copper, nickel, and iron clusters, where multiple isotopes make the mass spectra somewhat less revealing.

A. Carbon monoxide chemisorption

We begin with the chemisorption of carbon monoxide, in many respects the simplest reaction considered. With every metal we have investigated (including most of the metals discussed in this paper) carbon monoxide was found to readily chemisorb on all clusters with more than two atoms. For example, Fig. 1 displays a limited region of the time-of-flight

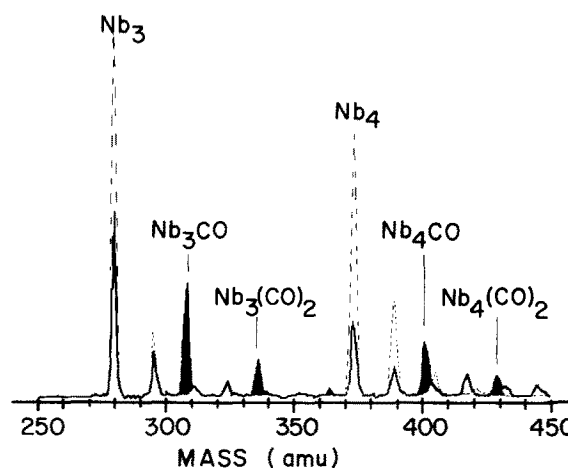


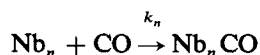
FIG. 1. Reaction study of small niobium clusters with CO. The dashed mass spectrum is that of the control experiment where only pure helium was injected into the reaction tube. The solid trace was observed when 2.4 sccm ($\text{cm}^3 \text{ atm/min}$) of CO was injected (with a pure helium carrier) into the reaction tube. The features growing in due to formation of $\text{Nb}_n(\text{CO})_m$ reaction products are blackened for emphasis. Corresponding reaction products for the Nb_nO cluster oxides are observable as small peaks on the base line.

mass spectrum for niobium clusters reacting with CO. The figure shows both the mass spectrum of the metal cluster beam with only pure helium injected through the reactant needles (the control spectrum) as well as the spectrum when CO was injected into the reaction tube. As shown in the figure, both the niobium trimer and tetramer react readily, producing a depletion of the parent bare cluster signal. In this case of CO chemisorption the ionization signal lost in the bare metal cluster channel reappears in higher channels in the form of $\text{Nb}_n(\text{CO})_m$ reaction products with $m = 1-3$. Although now shown in Fig. 1, all higher clusters of niobium were found to react with CO in a similar manner. With the limited mass resolution it was impossible to follow the successive additions of CO's to each cluster beyond three, but, at least up to this extent of reaction, all niobium clusters show the same tendency to chemisorb multiple CO molecules.

In stark contrast with this ready reaction for the higher clusters, the Nb atom and dimer were found to be remarkably inert. Even with far higher concentrations of CO than used in Fig. 1, no significant reaction of Nb or Nb_2 was observed. In reactions of atoms and dimers, however, we cannot claim a lack of apparent reaction is necessarily significant. These are gas phase addition reactions where thermalizing collisions with the helium buffer gas are essential to take away the energy of reaction and stabilize the reaction product. As discussed in paper I, the 50–100 Torr, 320 K helium buffer gas conditions of the reaction tube provide thermalizing helium collisions with reaction products

on the order of once every few nanoseconds. In the case of the larger clusters, the unimolecular decomposition time of the reaction complex is certainly much longer than this, and the required bath gas collisions will always occur prior to decomposition. In the case of clusters with only a few atoms, on the other hand, the absence of observable reaction products may simply mean that the reaction complex is too short lived to survive into the final expansion region where cooling occurs. In the case of $\text{Nb}_2 + \text{CO}$, a rough estimate of the lifetime of the Nb_2CO reaction complex (assuming a binding energy of 1 eV, and 200 cm^{-1} of energy above the dissociation threshold) shows the observed absence of reaction here is on the verge of being significant: the calculated lifetime (RRK) is on the order of 10^{-7} s. Since so little is presently known with certainty about the critical parameters that go into such a lifetime calculation for a metal cluster—CO complex, we prefer to err on the conservative side, and not draw any firm conclusions as to the reactivity of the atom and dimer for any of the metals and reaction partners considered in this study.

As stated at the outset of this section, CO chemisorption on metal clusters was found to be generally facile, with very little change as a function of cluster size. This can be seen in Fig. 2, which plots a coarse estimate of the relative reaction rates for CO chemisorption as a function of cluster size for both niobium and cobalt clusters, obtained from a series of mass spectra taken at various CO concentrations. These relative rate data are based on the following simple model. The chemisorption reaction for Nb_n is assumed to proceed in a single elementary step of the form



for which the elementary rate expression is

$$\frac{d[\text{Nb}_n]}{dt} = -k_n[\text{Nb}_n][\text{CO}].$$

Assuming that CO is in such excess that its concentration change is negligible, integration gives an expression for the rate constant, k_n , in terms of the measured fraction of Nb_n left unreacted (D_n), CO concentration ($[\text{CO}]$), and reaction time (t):

$$k_n = -([\text{CO}]t)^{-1} \ln D_n,$$

where

$$D_n = [\text{Nb}_n]_{\text{reaction}} / [\text{Nb}_n]_{\text{control}}.$$

For these initial survey studies of cluster chemisorption reactions, we have only a rough knowledge of the average CO concentrations and reaction times appropriate to the fast-flow reactor. Although it is possible to make reasonable estimates of these parameters and arrive at a coarse measure of the absolute reaction rates, k_n , we have far more confidence in taking the ratio of the reaction rate for the n th cluster to that for some reference cluster measured in the same mass spectrum. For this reason the rates plotted in this paper for the various chemisorptions studied are relative reaction rates,

$$R_n = \ln D_n / \ln D_r,$$

where D_n is the measured unreacted fraction of the n th clus-

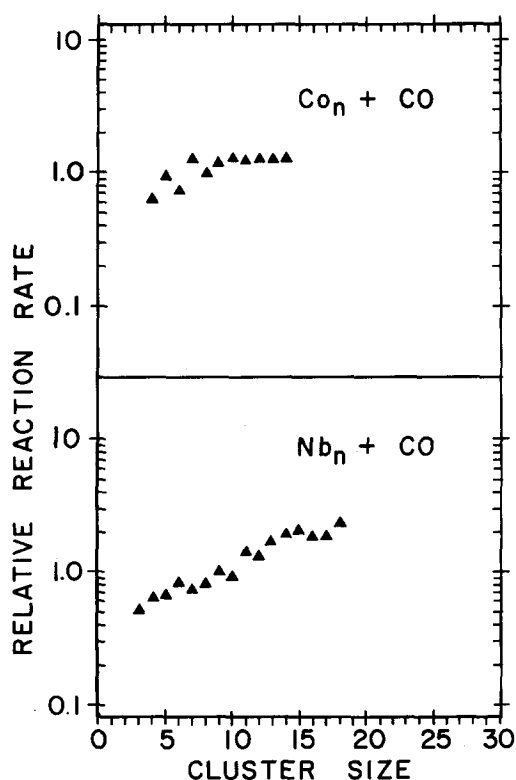


FIG. 2. Relative reaction rates for CO chemisorption for cobalt and niobium clusters. Estimated error bounds for these relative rate measurements are $\pm 20\%$.

ter, and D_r is the corresponding unreacted fraction of a reference cluster.

For the data in Fig. 2, Co_8 and Nb_9 were chosen as the reference clusters for the upper and lower panels, respectively. The measured relative reaction rates are observed to increase gradually with increasing cluster size, the rate of increase differing a bit between the two metals.

As discussed in Sec. II, these mass spectra were obtained by direct photoionization with the 7.9 eV output of a F_2 excimer laser at a fluence in the range of 0.1–0.5 mJ/cm^2 . This fluence is low enough to ensure that the vast majority of the ion signal comes from direct one-photon ionization with very little likelihood of the product photoion absorbing a second photon. Although fragmentation is always a concern, our experience is that direct F_2 laser excitation ordinarily photoionizes metal clusters and metal cluster adducts cleanly to produce the parent ion. In the present application of monitoring reaction with CO, this photoionization identifies that chemisorption has occurred, but does not answer the far more interesting question of whether the chemisorption is molecular, with CO remaining intact on the cluster, or dissociative, with the production of partially or even totally separated C and O atoms on the cluster surface. The resolution of this more interesting question must wait for more subtle probes such as direct laser excitation of the C–O

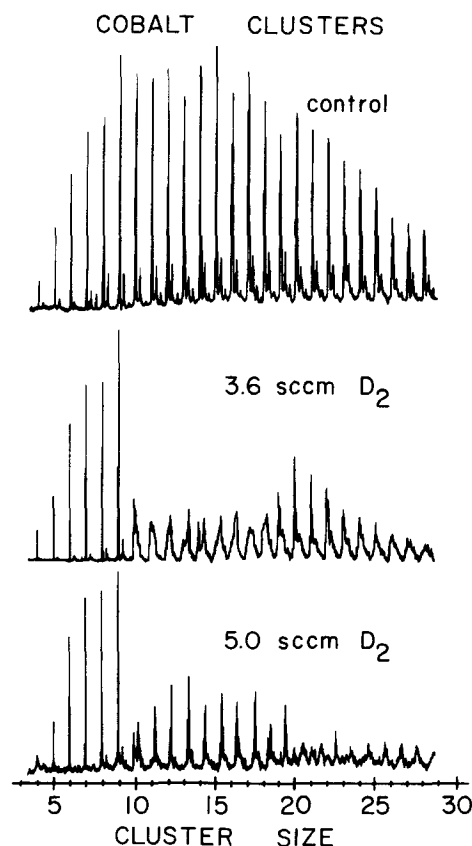


FIG. 3. Chemisorption study of D_2 on cobalt clusters. The control mass spectrum was performed with only pure helium injected as the reactant gas. The lower two mass spectra were taken with 3.6 and 5.0 sccm flow of injected D_2 reactant, respectively. See Figs. 4 and 5 for closer detail. The sharp peaks seen in the bottom-most trace for clusters with more than 10 atoms are all due to cobalt clusters with more than one molecule of D_2 chemisorbed.

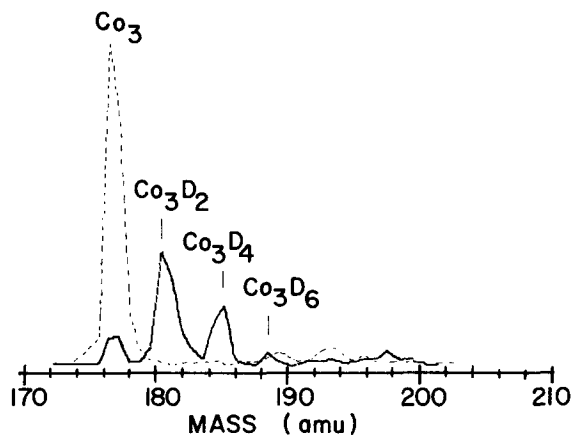


FIG. 4. Detail of the D_2 chemisorption experiment on Co trimer. The dashed mass spectrum is the control experiment (only pure helium as the reactant), the solid trace is the observed mass spectrum with an average reactant flow of 7.4 sccm D_2 . Note that only reaction products with even numbers of deuterium atoms are observed. Careful examination of the base line reveals that the Co_3C carbide and Co_3O oxide which are produced in small amounts in the laser plasma of the cluster source also chemisorb D_2 strongly.

stretch followed by multiphoton IR dissociation.

All in all, there is little in these CO chemisorption data to suggest that anything particularly dramatic is changing as the size of the metal cluster increases. Either there is little difference among metal clusters in this size range, or CO chemisorption is not a very discriminating probe.

One indication that CO is not very discriminating can be found in Fig. 1, where careful examination of the small peaks near the base line shows that the extent of CO chemisorption for the various niobium cluster oxides is much the same as the corresponding bare niobium clusters. These oxides are formed in the high temperature plasma of the laser vaporization cluster source from trace oxygen contaminants in the helium carrier gas. Certainly the addition of an oxygen atom to a small metal cluster like Nb_3 produces a major reorganization of the electronic structure. Nevertheless, CO chemisorption occurs as if nothing had changed.

B. Dissociative chemisorption of D_2 on cobalt clusters

Despite the above indication from CO chemisorption that there was little difference between one cluster and another, there are other reactions for which different sized clusters are actually *very* different. The first indication of this came in a study of the chemisorption of D_2 on bare clusters of cobalt, which appeared as a Communication earlier in this Journal.² Figure 3 shows a more extensive series of mass spectra for this important reaction. As seen in the figure, the bare clusters display very dramatic size dependences in their reaction with D_2 . Note particularly the rapid onset of high reactivity on going from 9 to 10 atoms per cluster. These variations in reactivity of metal clusters are the most abrupt and dramatic differences yet observed in *any* property as a function of cluster size.¹⁹

As with CO chemisorption, reaction with D_2 was not found to occur on the bare cobalt atom or diatom, Co_2 .

Again, it is not clear whether this is a simple kinetic effect associated with the short lifetime of the reaction complex or whether these species are inherently unreactive. The cobalt trimer, however, does react strongly. Figure 4 shows this trimer region in sufficient detail to resolve individual reaction products produced by the successive addition of up to three D_2 molecules.

As is evident in Fig. 4, there is no indication of any cluster species containing an odd number of deuterium atoms. This is not surprising in view of the strength of the D_2 bond—the chemisorption event would have to be incredibly exothermic, releasing 104 kcal per metal–hydrogen bond, in order to permit the ejection of a single D atom without gaining any other new bonds in the process.

The lower panel of Fig. 3, taken with a fairly high D_2 concentration is misleading when the figure is reduced to small size. It looks as though the bare clusters in the 10–20 atom size range have returned, as though the reactivity were less at higher concentrations than at lower ones. In a sense, this is just what has happened. The sharp peaks that look like the bare clusters are actually shifted to higher mass because the clusters have picked up a certain number of D_2 molecules and then stopped reacting. This titration-like behavior is shown in more detail in Fig. 5 where the control and D_2 reaction mass spectra are superimposed for clusters in the 9 to 16 atom range. Here the mass shift for each cluster is clear enough to permit a measure of the number of D_2 molecules required to saturate the cluster: 5 for Co_{11-12} , 6 for Co_{13-14} , and 7 for Co_{15-16} .

There is also some indication in this reaction data that the presence of D_2 on the cobalt cluster promotes further reaction with additional D_2 molecules, up to the fully saturated limit. As shown in Fig. 3, there is only a small concentration range over which clusters with intermediate amounts of chemisorbed D_2 are observed. This may be due to an increase in the effective reaction rate after adsorption of the first D_2 molecule. This point should be verified in more detail when later, more quantitative versions of these cluster

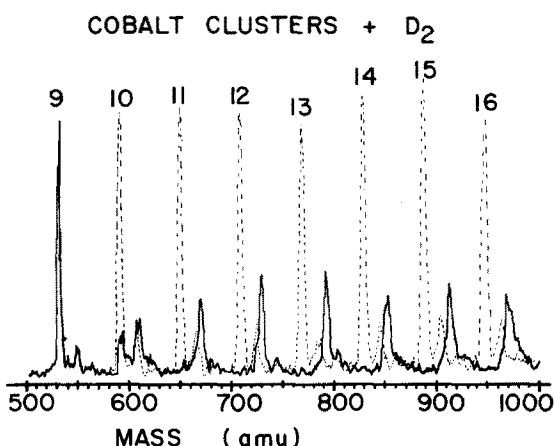


FIG. 5. Detail of D_2 chemisorption experiment in the 9–16 atom cluster range showing evidence for titration behavior in the chemisorption reaction. The dashed mass spectrum corresponds to the pure helium control experiment, the solid trace to a flow of 5.0 scmm D_2 injected into the reaction tube. The D_2 chemisorption process appears to shut off at five molecules of D_2 for Co_{11} and Co_{12} , six for Co_{13} and Co_{14} , and seven for Co_{15} and Co_{16} .

chemisorption experiments are available.

Chemisorption of D_2 is particularly interesting in that there is only one plausible way for the D_2 to bind to the cluster tightly enough to survive passage through the reaction tube and be observed in the molecular beam: D_2 must *dissociatively chemisorb*. Remember that the reaction products, whatever their nature, are exposed in the reaction tube to 50–100 Torr helium buffer gas at a temperature near 320 K. In paper I it was argued that any reaction product will be thermalized to the buffer gas temperature within a few microseconds. Under these highly collisional conditions at room temperature only strongly chemisorbed species will remain on the clusters. Their rate for desorption should be well approximated by an Arrhenius expression

$$k_{\text{desorption}} = A \exp(-E_a/RT),$$

where E_a is the heat of desorption, R is the gas constant, and T is the cluster temperature (320 K). This is just the approach used in the highly useful surface chemistry technique of thermal desorption,²⁰ where a large body of data has been accumulated in the application of this equation to wide ranges of real molecular desorptions. It is usually found that the preexponential factor, A , is on the order of 10^{14} to 10^{15} s^{-1} for surface desorptions. This value of 10–100 times larger than usually encountered in simple gas phase molecular decompositions, a fact that Zeiri, Redondo, and Goddard have ascribed to hindered rotations of the chemisorbed molecule on the bulk surface.²¹ In the case of small clusters with only 2 to 30 atoms, we have not yet reached the bulk surface limit, so an intermediate preexponential factor of 10^{14} seems reasonable.

For many of the clusters shown in Figs. 3, 4, and 5 the extent of reaction with the D_2 is nearly complete: essentially all bare cluster signal has been replaced by reaction product. Since the reaction tube has a residence time of 150–200 μs , the typical reaction product we see in the beam must have survived in the reaction tube for at least 80 μs without the D_2 desorbing from the cluster. The desorption rate must therefore be slower than 10^4 s^{-1} . The Arrhenius equation and this maximum desorption rate together imply that the minimum heat of desorption for a reaction product to be stable in the reaction tube is approximately 13 kcal mol^{-1} .

Hydrogen chemisorption is one of the best known of all surface chemistries.^{4–15,22} There are known molecular chemisorption states on some transition metal surfaces, but these are very weakly bound and are stable only at cryogenic temperatures. All known room temperature chemisorption states of H_2 on transition metal surfaces are dissociative, with the two hydrogens well separated at different binding sites on the surface.^{8,23}

The relative rates measured in these gas phase fast-flow experiments with D_2 on metal clusters reflect variations in the activation barrier to dissociative chemisorption. This is a nontrivial reaction that requires the concerted weakening of the strong H–H bond while simultaneously making two new bonds to the metal cluster. Transition metals are uniquely capable of such chemistry,⁸ and in these experiments we are beginning to see the onset of this behavior on the surface of small clusters.

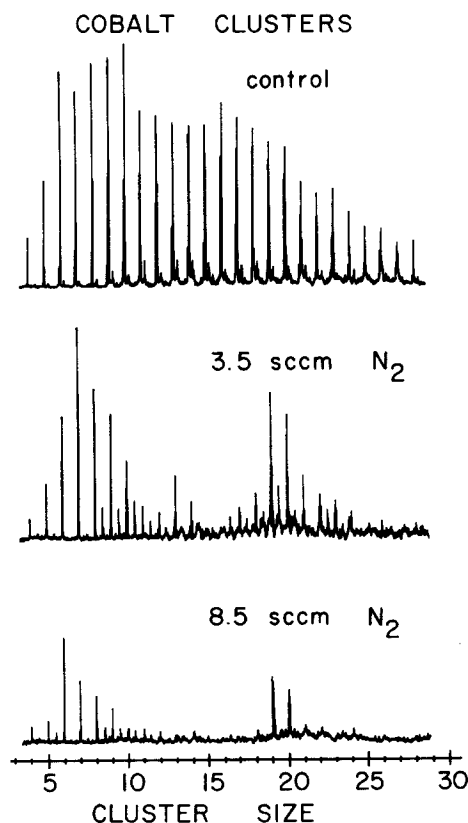


FIG. 6. Chemisorption study of N₂ on cobalt clusters. Careful examination of the mass spectra (particularly the middle trace taken with 3.5 sccm flow of N₂) reveals features due to reaction products with one or more N₂ molecules chemisorbed on the cobalt clusters. The higher concentration trace at the bottom is a particularly graphic demonstration of the comparative inertness of Co₁₉ and Co₂₀.

C. Dissociative chemisorption of N₂ on cobalt clusters

A fascinating parallel to these D₂ chemisorption studies is a related study using N₂. Figure 6 shows a characteristic mass spectrum for a control experiment along with spectra for two different concentrations of N₂ in the reaction tube. It is a bit difficult to see the details, but it is clear at a glance that the reactivity pattern obtained with N₂ is similar to that observed in Fig. 3 for reaction with D₂. Now, however, the sharpest change in reactivity is clearly in the vicinity of Co₁₉ and Co₂₀.

This similarity of reactivity patterns is quite clearly seen in Fig. 7, which plots the measured relative reactivities as a function of cobalt cluster size for both the D₂ and N₂ chemisorption reactions. These relative reactivity plots were obtained from measured depletion ratios for each cluster as seen in a variety of experiments at different concentrations—much as described previously for the Co chemisorption experiments. Although we have endeavored to make these as accurate as possible, the reader is cautioned not to take these relative rate measurements too literally. We have not plotted the estimated error bounds in the relative rate figures because these errors are highly correlated and inclusion in the figure simply makes it more difficult to see the reactivity pattern. The estimated error bounds range from $\pm 20\%$ for relative rates near unity to over 100% for some of the ex-

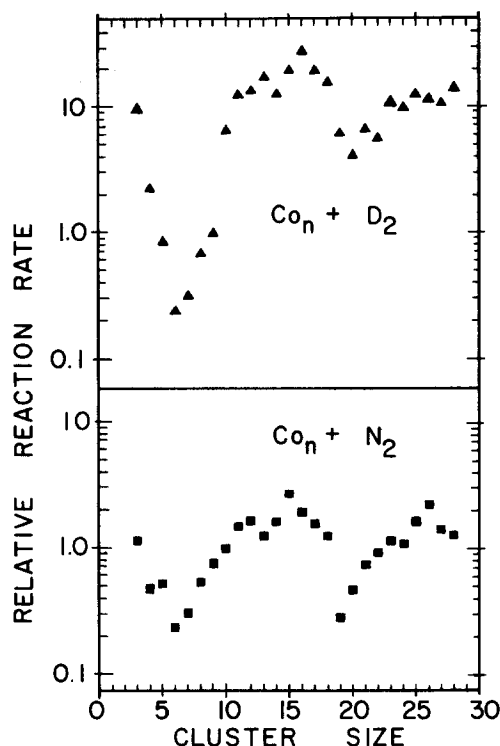


FIG. 7. Relative reaction rates of cobalt clusters with D₂ and N₂. Note the striking similarity in the reactivity patterns for these two reactants. The estimated errors for these relative rates is $\pm 20\%$ except for rates greater than 10 or less than 0.1 compared to the reference rate; for these extreme rates the measurements are only of semiquantitative significance.

treme points corresponding to clusters with either far faster or far slower reaction rates, as compared to the reaction rate of the reference cluster. The effect of these errors has been to smooth out the extremes. When more accurate reaction rate data is obtained we expect the patterns seen here to be even more pronounced.

The reactivity pattern seen in Fig. 7 for D₂ and N₂ chemisorption on cobalt clusters is particularly interesting when one recalls how little variation in reactivity was observed in CO chemisorption on these same clusters (see Fig. 2). Without question, the mechanism of N₂ chemisorption is more similar to the dissociative chemisorption of hydrogen (deuterium) than it is to the (presumably) molecular chemisorption of CO.

As with D₂, chemisorption of N₂ is known to be largely a dissociative process on transition metal surfaces at room temperature. Single crystal data is not yet available for N₂ adsorption on cobalt, but a great deal has been learned recently about the adjacent elements in the periodic table, iron and nickel. The tightest bound *molecular* form of N₂ now known on an iron single crystal surface is the σ adsorption state on the Fe(111) surface.²⁴ This σ state is bound by 31 kJ mol⁻¹, has a markedly reduced N--N vibration frequency (1490 cm⁻¹ as compared to 2194 cm⁻¹ for free N₂), and is believed to be π -bonded parallel to the surface. This molecularly bound σ state partially desorbs at 170 K, the remainder dissociating to form a surface nitride. In the case of nickel, recent angle resolved photoemission data have shown that

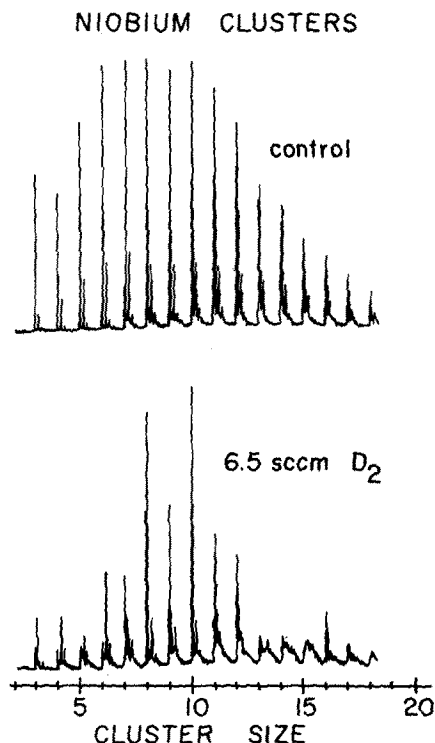


FIG. 8. Chemisorption study of D_2 on niobium clusters. Note the negligible reactivity of Nb_8 , Nb_{10} , and Nb_{16} , and the absence of titration behavior in the strongly reacting clusters.

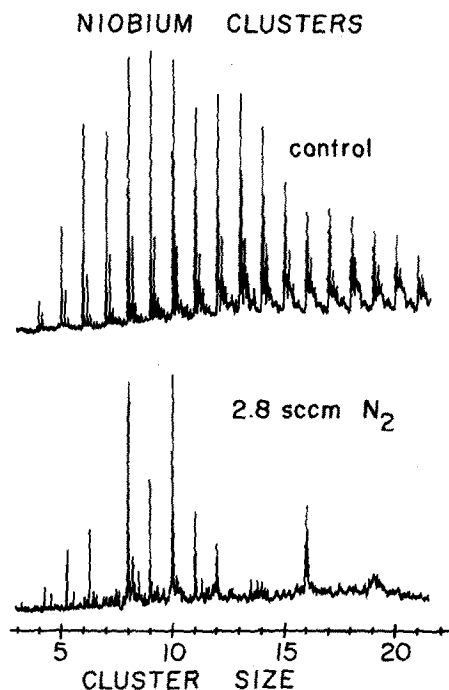


FIG. 9. Chemisorption study of N_2 on niobium clusters. The sharp peaks in the small cluster region of the lower mass spectrum are due to the N_2 chemisorption product, whereas the peaks seen in roughly the correct position for the 8–12 and 16th cluster of niobium are, in fact, due to the unreacted bare cluster.

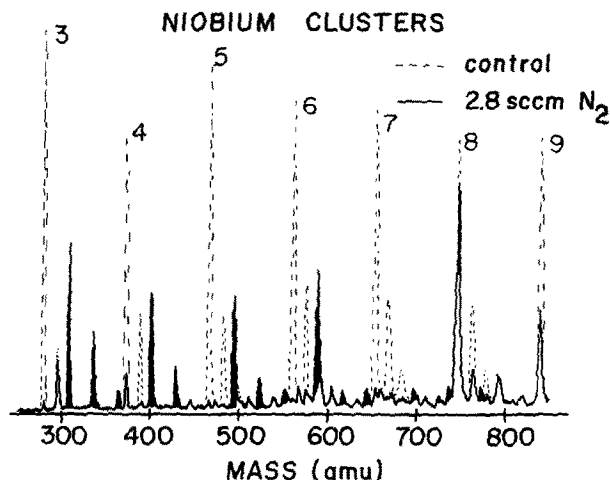


FIG. 10. Detail of the small cluster region of the N_2 chemisorption study on niobium. Peaks due to N_2 chemisorption reaction products have been blackened for emphasis. Note that the reactivity of the Nb_nO oxides is often markedly different from the corresponding pure niobium clusters—see the Nb_3 and Nb_8 clusters particularly in this regard.

the γ adsorption state of N_2 on $Ni(100)$ is molecularly adsorbed perpendicular to the surface.²⁵ This also is too weakly bound to survive at room temperature—it desorbs at only 140 K. Even though no data is yet available in the case of cobalt, it is reasonable to expect that it too exhibits only weak binding for molecular N_2 . For these reasons, the 320 K adsorption data for N_2 shown in Figs. 6 and 7 likely refer to a dissociative chemisorption process.

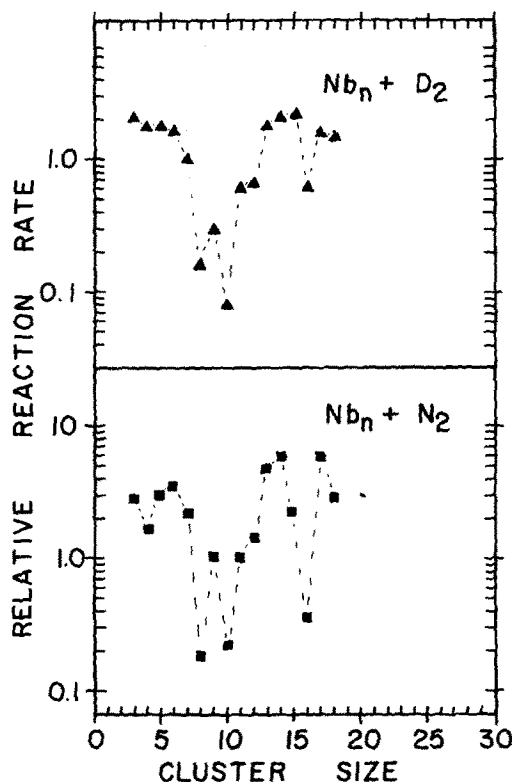


FIG. 11. Relative reaction rates of niobium clusters with D_2 and N_2 . Note the similarity in the reactivity patterns for these two reactants. Estimated error bounds for these relative rates are $\pm 20\%$ except for the extremely low and high reactivity points which are only semiquantitative.

D. Chemisorption of D₂ and N₂ on niobium clusters

Results from the extension of these D₂ and N₂ chemisorption experiments to niobium clusters are presented in Figs. 8–11. Once again dramatic changes in reactivity are observed as a function of cluster size. For both the D₂ and N₂ chemisorptions the clusters with 8, 10, and 16 atoms are far less reactive than clusters with only one atom more or less. Figure 10 presents a particularly clear view of these sharp reactivity differences for N₂ chemisorption on niobium clusters in the 3–9 size range. Note, for example, that the bare niobium trimer has nearly disappeared from the mass spectrum, the missing ion signal reappearing in peaks corresponding to Nb₃N₂, Nb₃N₄, and Nb₃N₆. In sharp contrast, the Nb₈ cluster has been largely unaffected by the N₂ reactant.

Also note that the reactivity of the corresponding cluster oxides is often sharply different than the bare metal cluster. Nb₃O, for example, is seen in Fig. 10 to be far *less* reactive than Nb₃, while Nb₈O is far *more* reactive than Nb₈. In direct contrast to the observations for CO chemisorption, the pattern of reactivity of the niobium cluster oxides for D₂ and N₂ chemisorption is quite different from that of the bare clusters.

The relative reaction rates measured as a function of cluster size for D₂ and N₂ on niobium are presented in Fig. 11. Again we emphasize that the errors in these measured relative rates are considerable. Particularly for the very fast and very slow relative rates, the measured values are likely to be biased due to the difficulty in measuring very large and very small depletions. Very slow relative rates tend to be overestimated, very fast rates tend to be underestimated. However, the gross pattern of reactivity, is well determined by the current measurements.

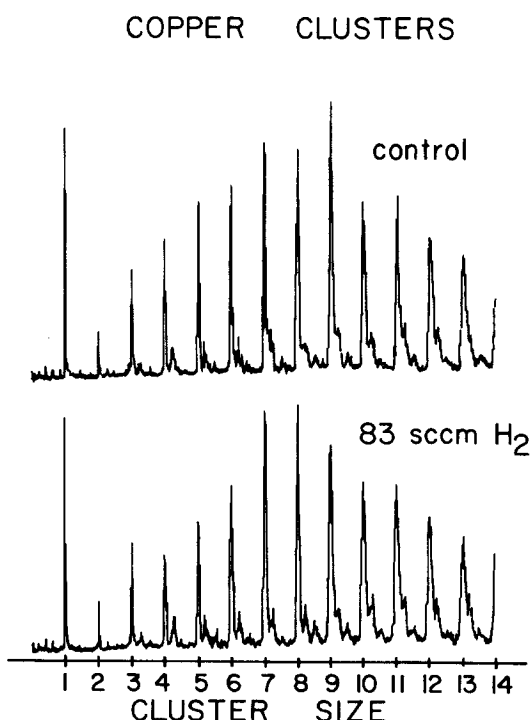


FIG. 12. Chemisorption study of H₂ on copper clusters demonstrating no significant evidence of reaction.

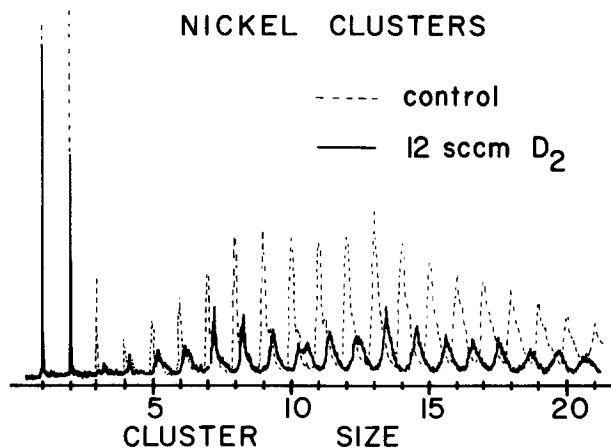


FIG. 13. Chemisorption study of D₂ on nickel clusters. The dashed mass spectrum pertains to the control experiment using only pure helium as a reactant; the solid line is the spectrum obtained with a reactant flow of 12 sccm D₂.

E. Copper clusters—A check for hydrogen chemisorption

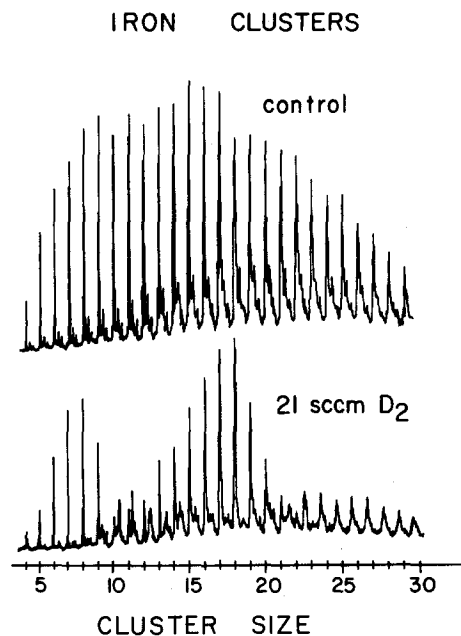
Dissociative hydrogen chemisorption is a surface chemistry that is peculiar to transition metals with open *d* shells.⁸ Copper is an interesting test case since the 3*d* band is fairly narrow and situated below the Fermi level.²⁶ Molecular hydrogen is known to chemisorb on copper surfaces, but this process possesses an activation barrier in the range of 3 to 5 kcal/mol, depending upon the crystal face.²⁷ Calculations of the electronic structure of copper clusters indicate the 3*d* band remains narrow and filled, lying well below the Fermi level,²⁸ so it is reasonable to expect that copper clusters will be unreactive toward H₂.

As a consistency check on our interpretation of the D₂ chemisorption experiments with cobalt and niobium clusters, we therefore extended the hydrogen reaction studies to copper clusters. Figure 12 shows the result of this experiment. As expected, no evidence of reaction was observed with H₂ (which should react faster than D₂) at a concentration over an order of magnitude higher than used in the previous experiments with cobalt and niobium.

F. Nickel and Iron cluster chemisorption experiments

Nickel is a particularly important transition metal for detailed cluster beam studies since it is by far the easiest of the open *d*-shell transition metals to handle in quantum chemical calculations. Figure 13 shows the result of a D₂ chemisorption experiment on nickel clusters using the new fast-flow reactor. Deuterium is found to chemisorb readily, but displays only a mild, nearly monotonic increase in reaction rate as a function of cluster size. In light of the dramatic effects seen with cobalt and niobium clusters, smooth reactivity variation with cluster size is rather surprising. Due to time constraints on the molecular beam apparatus, no other chemisorption experiments were done for nickel.

Iron completes the list of metals we have explored in these first chemisorption experiments with the new apparatus. Figure 14 presents mass spectra from a D₂ chemisorp-

FIG. 14. Chemisorption study of D₂ on iron clusters.

tion experiment. Once again, a highly size-dependent reactivity pattern is found for dissociative D₂ chemisorption. Relative rates abstracted from experiments such as these have been plotted along with similar data from the nickel chemisorption experiments in Fig. 15. The hydrogen-iron cluster reactive system has recently been investigated in a series of impressive papers by Riley *et al.*^{18(d),18(e)} The general pattern of absolute reaction rates determined in their experiments is in close accord with our relative rate measurements,

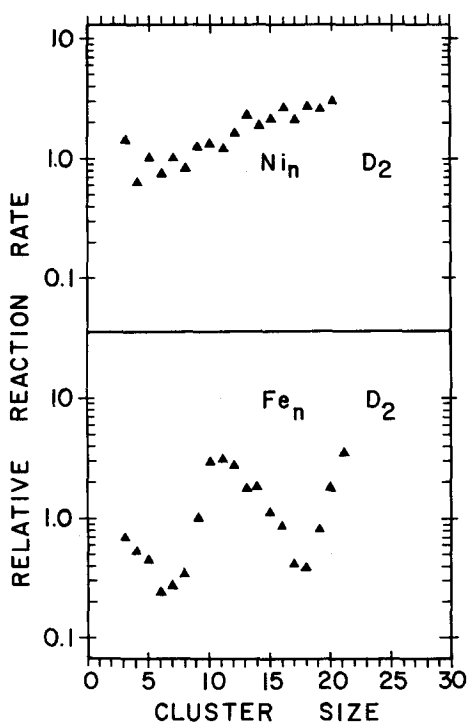
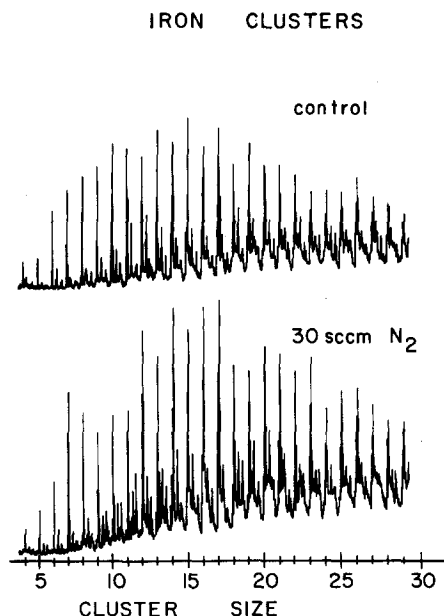
FIG. 15. Relative reaction rates for nickel and iron chemisorption rates with D₂.

FIG. 16. Chemisorption study of N₂ on iron clusters. The lower trace was taken with sufficient N₂ flowing into the reaction tube to lengthen the arrival time of the clusters by 30–40 μ s. Even so, very little reaction is evident here. Looking closely, there is clear evidence of new peaks growing in at 28 amu to higher mass of some of the bare clusters—particularly in the region of Fe₁₁—due to some formation of N₂ chemisorption products. The satellite peaks seen at 16 and 32 amu to higher mass of the bare ion clusters in these mass spectra are due to iron cluster oxides made in the laser plasma of the cluster source.

but spans a greater range in absolute magnitude. This is to be expected given our difficulty in measuring very large or very small depletions relative to our reference cluster, and does not alter any of our conclusions in the current work.

An extensive attempt was made to measure the relative reactivity patterns for N₂ chemisorption on iron clusters. Iron clusters, however, are relatively inert to N₂ chemisorption. Figure 16 shows the result of one experiment where an order of magnitude higher N₂ concentration was used than in the experiments with cobalt and niobium clusters. Even at this high concentration there is only a slight indication of reaction (Fe₁₁, for example does show a weak but clear Fe₁₁N₂ feature growing at 28 amu to high mass in the lower spectrum of Fig. 16).

At the relatively high concentrations of injected N₂ reactant used in the experiment of Fig. 16, the cluster arrival time at the detector was observed to increase by 20–40 μ s, to a total flight time of 800 μ s (see paper I). An experiment with argon injected instead of N₂ revealed this time shift to be a kinetic effect associated with the heavier mass of the reactant gas as compared to the normal helium carrier. We do not fully understand as yet the detailed mechanism for this delay. Even at the highest reactant concentrations only a few percent of the total gas in the reaction tube was the injected heavy reactant—not enough to produce a significant lowering of the terminal beam velocity. Since the increase in cluster arrival time was greatest for the heavier clusters, the effect may be due to the heavier reactant gas being more effective in slowing and redirecting the heavy clusters in the post-shock region at the entrance of the reaction tube, thus

increasing the effective residence time prior to the main supersonic expansion.

Whatever the cause of the extra delay in the arrival time of the clusters at the detector, it did make it difficult to be precise about the extent of reaction of iron clusters with N_2 . It is clear, however, that the reaction rate is far slower than that observed in the cases of cobalt and niobium at much lower N_2 concentrations. Furthermore, those few cases where $Fe_n N_2$ reaction products are found in the highest concentration studies are just the clusters that were found to be most reactive in D_2 chemisorption.

These low reactivity results for N_2 dissociative chemisorption on iron clusters are in accord with the extensive single crystal studies of Ertl and co-workers in their studies of N_2 dissociation as the rate limiting step in ammonia synthesis on iron catalysts.²⁹ It will be fascinating to see if potassium has the same promoting effect on these small iron clusters as it does for the bulk metal surface.³⁰

IV. SUMMARY AND CONCLUSIONS

These new reactivity data contain some of the sharpest size dependences ever measured for any property of a metal cluster. Even without considering what such experiments can tell us about the nature of the reactions themselves, the fact that *any* measurement can show such strong variations as a function of cluster size is a good indication that the cluster beam source is preparing well-defined clusters which do not suffer wholesale fragmentation in the detection process. Given the extremely rapid cluster nucleation, growth, and thermalization rates present in the laser-vaporization nozzle source, a potential problem is that clusters of a given size might be produced in metastable conformations corresponding to different geometrical isomers. The variation in properties among different frozen conformations of a particular cluster could well mask any sensible variation as a function of cluster size.

Luckily this is not the case. The relative reactivity data for N_2 chemisorption on cobalt and niobium clusters, for example, are particularly sensitive to the number of atoms in the cluster. The 16th cluster of niobium is a particularly dramatic case, being over an order of magnitude less reactive than Nb_{15} or Nb_{17} , or any other cluster of nearly the same size. Although this is hardly definitive evidence, it is strongly suggestive that clusters in the 2 to 30 atom size range produced in these beam sources do have a well-defined structure with as profound an impact on the cluster surface chemistry as steps, kinks, and crystal face have on the chemistry of bulk single crystal surfaces.

It is particularly significant that these reactions are measured in the gas phase at a temperature near 320 K. This requires that any chemisorption reaction product must be bound by about 13 kcal/mol in order to be observed. In the case of molecular hydrogen (and D_2) there is only one type of chemisorption that produces a binding energy this strong: dissociative chemisorption. Even in the case of N_2 , this requirement of a heat of chemisorption of at least 13 kcal/mol is sufficient to indicate a dissociative process: the strongest known N_2 molecular chemisorption state on a transition

metal (N_2 on rhodium³¹) is completely desorbed by 300 K. The D_2 and N_2 chemisorption reactions measured here for the first time on the surfaces of these bare metal clusters are therefore almost certainly dissociative processes to produce strongly bound surface hydrides and nitrides.

Such dissociative chemisorptions of strongly bound, ordinarily unreactive closed shell molecules are among the most fascinating (and technologically important) surface reactions known. As such, they have been the subject of extensive theoretical and experimental research for many decades. The conventional wisdom is that the critical interaction involves electron donation from surface orbitals of the metal into the antibonding molecular orbitals of the diatomic.^{8,13,14} Since this involves partial electron transfer from the metal to the diatomic, it is reasonable to suppose that the reaction on a metal cluster surface would become more feasible as the ionization potential of the cluster decreased with increasing cluster size.

Such a correlation has been pointed out quite forcefully in a recent paper by Whetten, Cox, Trevor, and Kaldor for the case of H_2 and D_2 chemisorption on iron clusters.³² Using essentially the same techniques as those described in paper I of this series, they measured the relative rates of dissociative chemisorption for H_2 and D_2 on iron clusters in the size range from Fe_8 through Fe_{25} , and obtained roughly the same results as those reported here in Figs. 14 and 15. In previous, very careful work³³ they had already measured the ionization thresholds for these clusters and readily observed that the local *minimum* in D_2 chemisorption reaction rate near Fe_{17} and Fe_{18} (see Fig. 15) corresponds exactly with a local *maximum* in the measured ionization potential of these clusters as a function of cluster size. As demonstrated quite convincingly in their paper, this correlation between ionization potential and D_2 chemisorption rate is remarkably good in the Fe_8 – Fe_{25} cluster size range. There seems to be some truth, therefore, in the conventional wisdom that this dissociative chemisorption reaction requires metal $\rightarrow H_2$ electron donation in its rate-determining step.

This is certainly not the whole story, however. For example, the data presented in Figs. 14 and 15 reveal there are actually at least two minima in the D_2 reaction rate dependence on cluster size. The first occurs near Fe_6 (a region not reported in the work of Whetten *et al.*³²), and does not correlate with a local maximum in the ionization potential. In addition, the observed inability of copper clusters to dissociatively chemisorb D_2 (see Fig. 12) provides a graphic demonstration that ionization potential alone correlates very poorly with reactivity. Earlier work from this laboratory has studied the ionization potential behavior of copper clusters quite extensively.³⁴ Many of the copper clusters shown in Fig. 12 to be unreactive toward D_2 , have ionization potentials as low as the highly reactive iron clusters of Fig. 15. Finally, recent experiments bracketing the ionization potentials of cobalt and niobium clusters show no clear correlation of reactivity with ionization potential, and indeed, in some cases demonstrate an anticorrelation.^{17(f)}

The dissociative chemisorption behavior of metal surfaces towards molecular hydrogen has long been considered a chemistry unique to transition metals⁸—a fact that imme-

diately suggests that surface d orbitals must play an intimate role. This point has been examined in detail in the recent *ab initio* calculations of Siegbahn, Blomberg, and Bauschlicher,¹⁴ who modeled H_2 chemisorption on various surface sites of small nickel clusters both with and without the free use of $3d$ orbitals at the chemisorption site. As expected, $3d$ orbital participation was found to be crucial in lowering the activation barrier to the dissociative chemisorption event. From both the long term experience of experimentalists and recent high level theory, it appears likely that the critical character monitored in these dissociative D_2 chemisorption experiments is associated with the d character of the frontier orbitals on the surface of the metal clusters. Now that the size dependence of these reactions are known on metal cluster surfaces, theorists are presented with a new challenge and a new means of verifying their models of the electronic structure of metal surfaces, at least to the extent that this is probed by dissociative chemisorption rates.

Whatever turns out to be the critical factor enabling dissociative chemisorption of D_2 on these clusters, it is clear from the reactivity patterns reported here that the same sort of interaction is probably also critical in dissociative N_2 chemisorption. Although there are small but real differences between these results for D_2 and N_2 , the patterns of reactivity as a function of cluster size are far too similar to be accidental.

Carbon monoxide, on the other hand, shows a totally different pattern of reactivity. Unlike diatomic hydrogen and nitrogen, CO is known to *molecularly* absorb to a wide variety of metal surfaces with heats of desorption considerably in excess of the 13 kcal/mol threshold critical in these room temperature gas phase experiments.^{35,36} Although dissociative chemisorption of CO may occur on these clusters, as it does on many transition metal surfaces, the primary reactive step probably still involves molecular chemisorption, possibly followed by dissociation. The slow, monotonic increase in chemisorption rate observed here as a function of cluster size suggests that CO chemisorption is a considerably simpler, less demanding process than dissociative chemisorption of D_2 or N_2 .

Another indication that CO chemisorption is comparatively unselective is the fact that the cluster monoxides were found to chemisorb CO at roughly the same rate as the corresponding bare cluster. This is an example of what may become an effective means of probing the nature of surface reactions: derivativization of the surface with known groups. This has long been a classic technique in molecular chemistry, but rather difficult to apply in the study of bulk surface reactions. Now on the surfaces of these molecular clusters, these traditional small molecule chemical techniques should find a new life. In the case of CO chemisorption, the presence of oxygen atoms on the cluster leaves the reaction rate largely unaffected; the presence of oxygen critically affects the dissociative chemisorption of N_2 , however (see Fig. 10). For some clusters such as Nb_3 , presence of oxygen is an inhibitor, whereas for other clusters such as Nb_8 , oxygen has the reverse effect: it dramatically promotes the N_2 chemisorption event. In traditional catalysis research, as well as the more recent single crystal surface chemistry studies, there have

been extensive studies of additives which promote or poison a particular surface chemistry. Clearly this tradition may be expected to continue in the new molecular surface science of metal clusters.

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